

# REMOVAL OF AL- AND CA-NITRILOTRIACETIC ACID FROM WATERS BY SUBSOILS

Larry M. Shuman

*AUTHOR:* Department of Agronomy, University of Georgia, Georgia Experiment Station, Griffin, Georgia 30223-1797.

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## INTRODUCTION

Synthetic chelating agents and the metals they carry can be environmental pollutants. Chelating agents are organic molecules with two or more functional groups which bond metals by encircling them with ligand "arms". Metals, which would normally be stationary in soils and sediments, can be resolubilized and transported by chelating materials. Chelates are often used to scavenge metals in industrial processes and can carry metals into the environment. Preliminary research is needed to determine the kinetics of chelating agents being sorbed or degraded in order to further study the impact they, and the metals they carry, have on soils, sediments and waters. Chelating agents could have profound influences on the free toxic metal concentrations in waters in Georgia due to possible release from soils and sediments.

The objective of these experiments was to determine the kinetics of loss of nitrilotriacetic acid (NTA) from solution caused by two subsoils when the NTA was associated with either calcium or aluminum. These elements are being used in model validation studies for competition for Al and other metals among chelates, soil surfaces, and solution. Models such as MINTEQA2 are used by soil and environmental scientists to predict the amounts of chelated metal in soil solution which may be free to move in a soil column and ultimately find its way into ground and surface waters.

## MATERIALS AND METHODS

### Common Procedures for All 3 Experiments

The soils were a Cecil clay and a Fullerton clay loam subsoil which were air dried and sieved through a 2 mm screen. Nitrilotriacetic acid (NTA) was dissolved with KOH from the  $\text{Na}^+$  form and the pH adjusted to 4.5 with HCl. The chelate was saturated with  $\text{Al}^{3+}$  or  $\text{Ca}^{2+}$  by adding equimolar amounts of the appropriate cation solution with Cl as the anion. Equilibrations were carried out in triplicate in 125 mL Erlenmeyer flasks shaken on a rotary shaker at room temperature. Soil weight was 25 g and the solution was 50 mL. The pH was adjusted to 4.5

at the initiation of the equilibration period. Following equilibration, the solution was decanted, centrifuged, and filtered through Whatman #42 paper. NTA was analyzed using a colorimetric procedure which uses a Zincon color reagent (Thompson and Duthie, 1968). Sorbed NTA was desorbed by adding 75 mL of 0.025 M NaOH to the soil in the flasks, shaking for 1 hr, adding 7.5 mL 0.05  $\text{CaCl}_2$ , mixing, letting stand 15 min., and filtering. The NTA in this solution was measured as above.

### Individual Experiments

Three experiments were conducted, each designed to determine different kinetic information. The first was a short-term (2 hr) experiment using three NTA concentrations ( $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$  moles/L) to study only adsorption and exclude degradation. The second was a long-term (3 days) experiment using the same NTA concentrations with and without access to air in order to study degradation and whether lack of oxygen would inhibit degradation (Tiedje and Mason, 1974). Additional data were recorded including the pH and conductivity of the suspension at the end of the equilibration period. The final experiment was a long-term kinetic experiment with one NTA concentration ( $10^{-3}$  moles/L) using the following times to produce a kinetic sorption/degradation curve: 5 min., 30 min., 1 hr, 2 hr, 5 hr, 16 hr, 24 hr, 48 hr.

## RESULTS

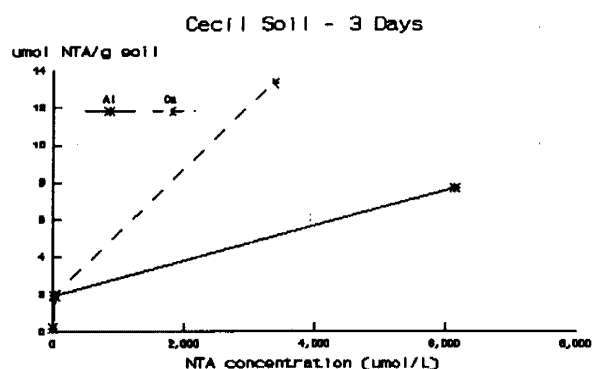
The Al-NTA lowered suspension pH by approximately 0.3 pH units, whereas Ca-NTA raised suspension pH, especially for the higher concentrations and longer time periods (Table 1).

The pH variations were greater in the Fullerton soil, which was lower in clay and organic matter than Cecil. The Cecil soil sorbed more NTA than Fullerton (data not shown). More Ca-NTA was sorbed than Al-NTA at 2 hr and 3 days, but differences were greater for Cecil than Fullerton soil (Figs. 1 and 2). Very little difference in sorption occurred for the 2 hour versus the 3 day time periods, indicating that the underlying processes were similar (Figs. 1 and 2).

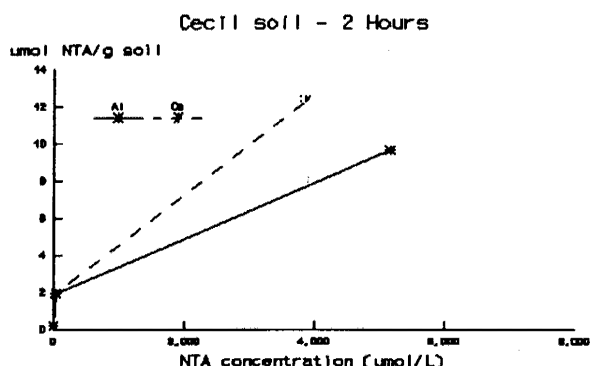
**Table 1. Soil pH After Equilibration With Al- or Ca-NTA For Either 2 Hours or 3 Days.**

NTA $\mu\text{mol/L}$	Al/Ca	Subsoil			
		Cecil		Fullerton	
		2 hr	3 days	2hr	3 days
$10^{-4}$	Al	4.66a <sup>†</sup>	4.59b	4.25a	4.57a
	Ca	4.73a	4.66a	4.29a	4.57a
$10^{-3}$	Al	4.45b	4.47b	4.18a	4.41b
	Ca	4.72a	4.64a	4.17a	4.47a
$10^{-2}$	Al	4.22b	4.18b	4.13a	3.63b
	Ca	4.66a	5.19a	4.02a	4.74a

<sup>†</sup>Means for Al vs. Ca within a soil, time, and NTA concentration followed by the same letter are not different at the 5% level according to an ANOV.

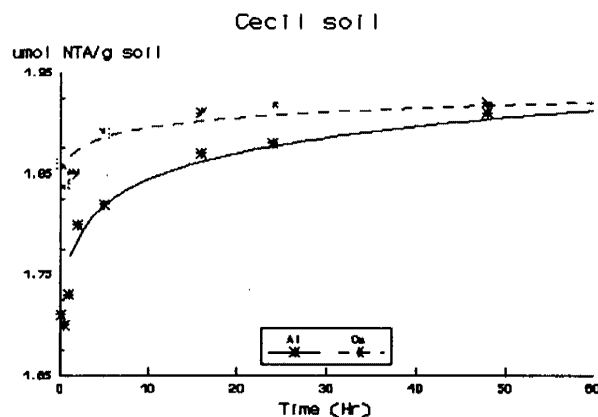


**Figure 1. Three day sorption for 3 rates of Ca- and Al-NTA for Cecil subsoil.**

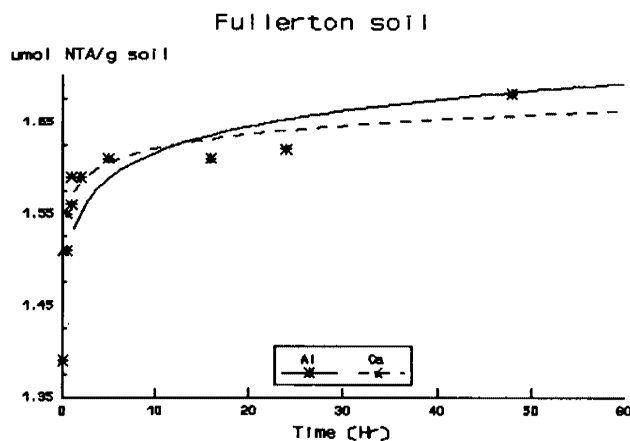


**Figure 2. Two hours sorption for 3 rates of Al- and Ca-NTA for Cecil subsoil.**

Anaerobic suspensions sorbed NTA in the same amounts as aerobic suspensions (data not shown), indicating that either degradation was by anaerobic processes or that degradation was not as important as adsorption. Desorption between soils and Al/Ca treatments were similar at 2 hr. At 3 days desorption was higher for Ca-NTA than Al-NTA at the highest concentration only (data not shown). Anaerobic conditions did not affect desorbed NTA significantly. Kinetic data show that for Cecil soil, near equilibrium was attained at about 16 hr and for Fullerton at about 5 hr. Sorption increased for both soils at 48 hr over that at 24 hr (Figs. 3 and 4), indicating that degradation may become important after one day. Tiedje and Mason (1974) also found that the biodegradation rate was negligible at times less than one day, especially for subsoils.



**Figure 3. Kinetics of sorption of Ca- and Al-NTA by Cecil soil.**



**Figure 4. Kinetics of sorption of Ca- and Al-NTA by Fullerton soil.**

## CONCLUSIONS

Ca-NTA was sorbed to a greater extent than Al-NTA providing evidence that in equilibrium model validations, differential sorption may affect predictions of free toxic metal concentrations in waters. Since aeration did not appreciably affect results, aerobic degradation is probably not as important as adsorption at the time periods studied. At low NTA concentrations, 90-100% was sorbed, showing that soil surfaces readily reduce NTA concentrations in soil water. Results indicate that sorption is rapid (within several hours) and that initial loss of NTA may be caused by adsorption followed by slower degradation processes. In model validation studies for metal-chelate equilibria in soils and waters, the differential sorption between cations should be taken into account and sorption plus degradation be considered as major mechanisms for loss from solution.

## ACKNOWLEDGMENTS

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## LITERATURE CITED

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- Tiedje, J. M., and B. B. Mason. 1974. Biodegradation of nitrilotriacetic acid (NTA) in soils. *Soil Sci. Soc. Am. Proc.* 38:278-283.